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The Arrhenius Acid and Base Theory

Shikha Munjal and Aakash Singh

Abstract

Swedish Svante Arrhenius, in 1884 proposed the concept of acid and base based on the theory of ionization. According to Arrhenius, the acids are the hydrogen-containing compounds which give H^+ ions or protons on dissociation in water and bases are the hydroxide compounds which give OH^- ions on dissociation in water. This concept is only applicable to those compounds which dissolved in aqueous solution (or you can say where water is the solvent). It covers many common acids, bases and their chemical reactions, but there are also other compounds that have the characteristics of acids and bases but they do not fit into Arrhenius concept.

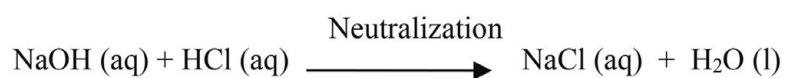
Keywords: acids and bases, Arrhenius acid-base theory, the water-ion system, amphoteric nature of water, hydrogen or hydronium ion

1. Introduction

The concept of acids and bases have been defined many times in different ways. Several scientists put various definitions to characterize the acids and bases in which some of the concepts are quite narrow and some are comprehensive. Acids and bases are existing everywhere in our daily life. Every liquid except water, that we used having acid and basic properties, for example, vinegar (contains acetic acid), soft drinks (contains carbonic acid), buttermilk (contains lactic acid), soap (contains base). The earliest definitions were made on the basis of their taste and their effect on other substances.

1.1 Acids

Acid are those substances which have sour in taste, sharp odor, corrosive, having $pH < 7$ and turn blue litmus red. The neutralization reaction occurs when acid reacts with alkali, forms salt and water. The products are less acidic or basic than reactants. It reacts with metals, produces H_2 . For example, the reaction between sodium hydroxide (base) and hydrochloric acid, forms sodium chloride (salt) and water.



1.2 Factors affecting acidic strength

The strength of acids and bases depends on following factors:

- Polarity of the molecule and strength of H–A bond
- Electro negativity
- Size

1.2.1 Polarity of the molecule and strength of H–A bond

As the polarity of the molecule increases, the electron density will get away from hydrogen atom and it becomes H^+ (proton). The greater is the positive charge on the hydrogen atom, H–A bond will become weaker, lesser is the energy required to break it. Then, the proton will easily dissociate in the solution. Hence, it will be the strong acid [1].



1.2.1.1 Key points

The priority should be given to the polarity of H–A bond, when we compare the acidic strength of elements in the same row. But when we compare the acidic strength of elements of same group of periodic table, then priority is given to strength of H–A bond.

1.2.2 Electro negativity

The hydrogen is attach to the more electronegative atom is more acidic. For example - the hydrogen is attached to the oxygen (E.N = 3.5) is more acidic than the hydrogen attached to nitrogen (E.N = 3.0, which is less electronegative than oxygen).

1.2.3 Size

The size of “A” atom affects the acidity of acidic strength. As the size of the atom increases, the bond becomes weaker and acidic strength increases [2].

1.2.4 Hybridization

Hybridization plays an important role in determining the acidic strength. As the hybridization moves from sp^3 to sp , the “s” character increases, so acidic strength increases.

1.3 Bases

Bases are those substances which have bitter taste, odorless, turn red litmus blue, having pH more than 7 and becomes less alkaline when react with acid. These are violent and less reactive than acids. For example, NaOH (Sodium hydroxide), LiOH (Lithium hydroxide), KOH (potassium hydroxide), etc.

These are the general properties of acids or bases, but not true for every single acid or base. There are some important concepts:

- Arrhenius acid-base theory
- Lewis acid-base concept

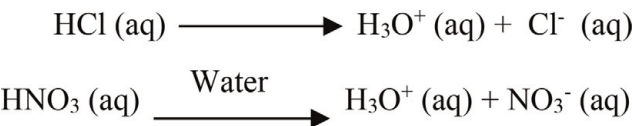
- Bronsted-Lowry concept
- Lux-flood concept
- Solvent-system concept

2. The Arrhenius acid-base theory (the water-ion system)

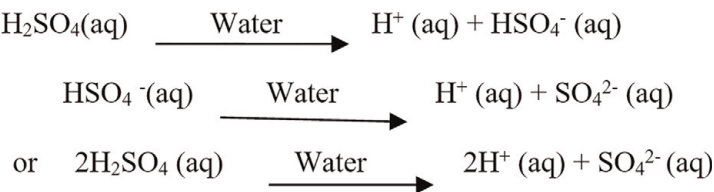
The Arrhenius acid-base theory was proposed by Swedish Svante Arrhenius. It was the first modern approach to acid-base concept. This theory is quite simple and useful. According to Arrhenius theory, acids are the compound that increases the concentration of H⁺ or proton in aqueous solution. The released H⁺ ion or proton is not free-floating proton, it exists in combined state with the water molecule and forms hydronium ion (H₃O⁺). The common examples of Arrhenius acid includes HCl (hydrochloric acid), H₂SO₄ (sulphuric acid), HNO₃ (nitric acid), etc. as shown in Table 1.



When it is dissolved in water, then:



The acids like HNO₃, HCl, etc. gives one proton on dissociation, called monoprotic acids. The acids like H₂SO₄, H₃PO₄, etc. which having more than one hydrogen atoms and gives more than 1 H⁺ ions on dissociation, called polyprotic acids. It is not necessary that polyprotic acids are stronger than monoprotic acids.



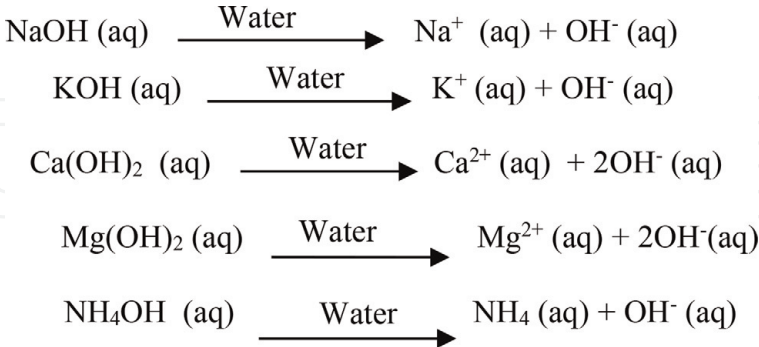
Similarly, Arrhenius bases are compounds that increase the concentration of OH⁻ or hydroxide ion in aqueous solution or having at least one OH⁻ ion in

Arrhenius acid formula	Name
HClO ₃	Chloric acid
HNO ₃	Nitric acid
HClO ₄	Perchloric acid
H ₃ PO ₄	Phosphoric acid
H ₂ SO ₄	Sulphuric acid
H ₂ SO ₃	Sulfurous acid
HCl	Hydrochloric acid
CH ₃ COOH	Acetic acid
HBr	Hydrobromic acid

Table 1.
Some Arrhenius acids.

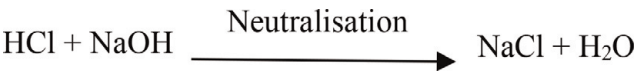
formula. The common examples of Arrhenius base includes NaOH (sodium hydroxide), KOH (potassium hydroxide), Ca(OH)₂ (calcium hydroxide), Mg(OH)₂ (magnesium hydroxide), NH₄OH (ammonium hydroxide), etc. as shown in **Table 2**.

When sodium hydroxide dissolved in water, it fully dissociates into ions Na⁺ and OH⁻, this dissociation increases the concentration of hydroxide ions in the solution.

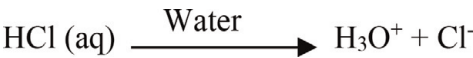


2.1 Neutralization reaction

When Arrhenius acid and Arrhenius base reacts, salt and water is formed as product, the reaction is known as neutralization reaction. For example:



The acids which are completely ionized in aqueous solution, is termed as strong acids such as HCl, HNO₃, H₂SO₄, etc.



Hydrochloric acid is a strong acid. When it dissociates into water, hydronium ion and chloride ions are formed as product. Chloride ions are weak base, but its basicity does not make the solution basic because acidity is overpowering the basicity of chloride ions. The H⁺ ions combine with water molecule and form hydronium ion. In case of strong acid, the concentration of hydronium ion formed is equal to the concentration of the acid whereas in case of weak acids, the concentration of hydronium ions in solution is always less than the concentration of hydrogen ions.

Arrhenius base	Name
NaOH	Sodium hydroxide
NH ₄ OH	Ammonium hydroxide
KOH	Potassium hydroxide
Mg(OH) ₂	Magnesium hydroxide
Ca(OH) ₂	Calcium hydroxide
Al(OH) ₃	Aluminum hydroxide

Table 2.
Some Arrhenius bases.

Whereas the acids which are weakly ionized in aqueous solution, is termed as weak acids such as acetic acid (CH_3COOH).



In case of weak acids, the concentration of hydronium ion is always less than the concentration of acid.

Similarly, bases which are completely ionized in aqueous solution, are termed as strong bases such as NaOH , KOH , etc. whereas the bases which are weakly ionized in aqueous solution, is known as weak bases such as ammonium hydroxide (NH_4OH), calcium hydroxide ($\text{Ca}(\text{OH})_2$), etc.

Note: It is not necessary that strong acids/bases are concentrated and weak acids/bases are dilute. Because, the dissociation of a substance does not depend on its concentration.

3. Utility of Arrhenius concept

This theory explains many phenomena like strength of acids and bases, salt hydrolysis and neutralization.

4. Hydrogen ion (H^+) or hydronium ion (H_3O^+)

When electron is removing from hydrogen atom, hydrogen ion H^+ is formed which is very reactive. But this H^+ ion does not exist in aqueous solution. Since in aqueous medium, it reacts with water molecule and forms hydronium ion (H_3O^+). Water is a polar molecule; it has the ability to attract the hydrogen ion (H^+). The water contains hydrogen and oxygen in which oxygen (EN = 3.5) is more electronegative that pulls the electron density towards it and causing the partial negative charge on the molecule. Due to partial negative charge, it has ability to attract the positively charged hydrogen ion (H^+) and form hydronium ion (H_3O^+). Hydronium ions are more stable than hydrogen ions.



The hydronium ion is very important factor in chemical reaction that occurs in aqueous solutions [3]. It is formed by the protonation of water.

5. Concept of pH

The pH of solution can be determined by the concentration of hydronium ion.

$$\text{pH} = -\log (\text{H}_3\text{O}^+)$$

From this equation, we can find the pH of pure water. The pH of pure water comes to be 7 that is considered to be neutral. The solution is either acidic or basic depending on the change in the concentration of hydronium ion.

According to **Figure 1**:

- If the concentration of the hydronium ion in the solution increases means more than 10^{-7} mol/l, pH increases that makes the solution more acidic.

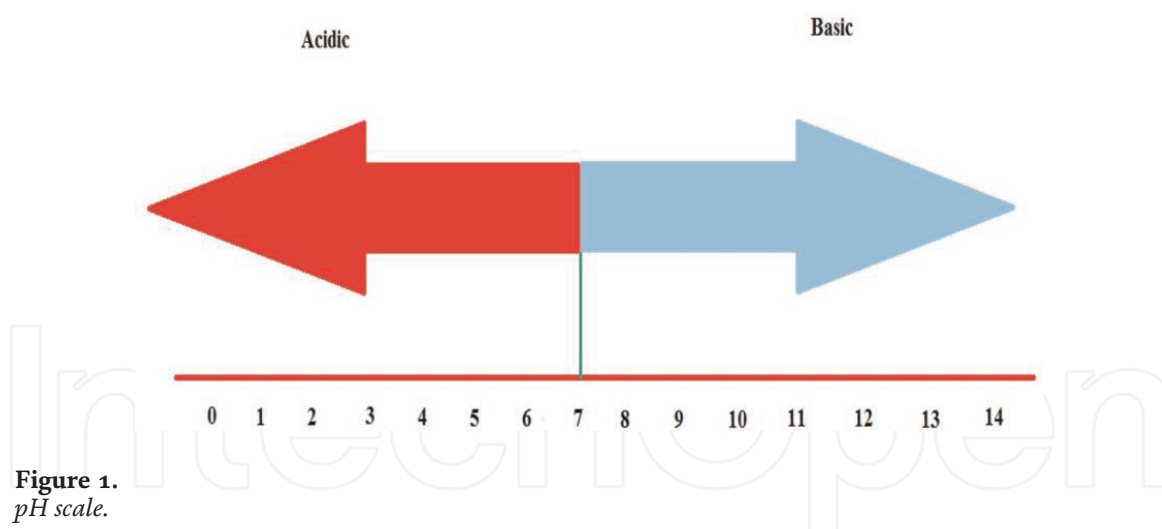


Figure 1.
pH scale.

- If the concentration of the hydronium ion in the solution decreases means $<10^{-7}$ mol/l, pH decreases that makes the solution more basic.

6. Amphoteric nature of water

The word amphoteric is derived from Greek word “amphi” that means both (acid and base). Amphoteric substances are those that has potential to act either as an acid or base. For example: H_2O (water) [3].

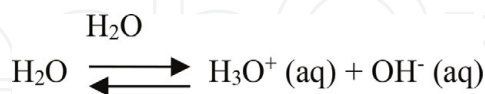


On dissociation, it ionizes into H^+ and OH^- (hydroxide) ion. The presence of H^+ indicates an acid and the presence of OH^- ion indicates a base. Since, water is a neutral molecule. So, it dissociates equally into H^+ and OH^- ion.

According to Arrhenius acid-base theory:

The amphoteric nature of water is very important because most of the acid-base chemical reactions takes place in the presence of water. Water is important amphoteric compound that can act as both an Arrhenius acid or Arrhenius base.

Auto-ionization of water [4];



The H^+ ion (a bare proton) does not exist in the solution, it forms hydronium ions by hydrogen bonding with nearest water molecule. Many books refers the “concentration of hydrogen ions” which is not correct. Because there are no H^+ ions, only hydronium ions in the solution. Technically, the number of hydronium ions formed is equal to the number of hydrogen ion. So, both can be used.

7. Advantages of Arrhenius theory

This theory is used to explains:

- Strength of acid and bases

The strength of Arrhenius acid and Arrhenius base can be determined by the extent to which it dissociate to give H^+ ion or hydroxide ion [5].

- The properties of acids and bases in aqueous medium.
- Neutralization of acid by reaction with base

8. Limitation of Arrhenius acid-base theory

1. This theory is very limited, out of three theories. According to this theory, the solution medium should be aqueous and acid should produce hydrogen ion (H^+) or base should produce hydroxide ion (OH^-) on dissociation with water. Hence, the substance is regarded as Arrhenius acid or Arrhenius base when it is dissolved in water. For example, HNO_3 is regarded as Arrhenius acid when it is dissolved in aqueous solution. But when it is dissolved in any other solvent like benzene, no dissociation occurs. This is against the Arrhenius theory.
2. Arrhenius theory is not applicable on the non-aqueous or gaseous reactions because it explained the acid-base behavior in terms of aqueous solutions.
3. In Arrhenius theory, salts are produced in the product which are neither acidic nor basic. So, this theory cannot explain the neutralization reaction without the presence of ions. For example, when acetic acid (weak acid) and sodium hydroxide (strong base) reacts, then the resulting solution is basic. But this concept is not explained by Arrhenius.
4. Arrhenius theory is only applicable to those compounds which have formula HA or BOH for acids and bases. There are some acids like $AlCl_3$, $CuSO_4$, CO_2 , SO_2 which cannot be represented by HA formula, this theory is unable to explain their acidic behavior. Similarly, there are some bases like Na_2CO_3 , NH_3 , etc. which do not have the BOH formula, this theory is unable to explain their basic behavior.

9. Bronsted-Lowry theory

We have been previously learned an Arrhenius acid-base theory which provided a good start towards the acid-base chemistry but it has certain limitations and problems. After this theory, a Danish chemist, named Johannes Nicolaus Bronsted and British scientist, Thomas Martin Lowry proposed a different definition of acid-base that based on the abilities of compound to either donate or accept the protons. This theory is known as Bronsted-Lowry theory, also called Proton theory of acid and base. This theory gives a more general and useful acid-base definition and applies to a wide range of chemical reactions. In this theory, we usually consider a hydrogen atom as a proton that has lost its electrons and becomes a positively charged hydrogen ion (represented by symbol, H^+).

According to Bronsted-Lowry concept, an acid is considered to be Bronsted-Lowry acid which is capable to donate a proton to someone else. A base is considered to be Bronsted-Lowry base which is capable to accept a proton from someone else. From here, it can be noted that when an acid reacts with a base, the proton is transferred from one chemical species to another.

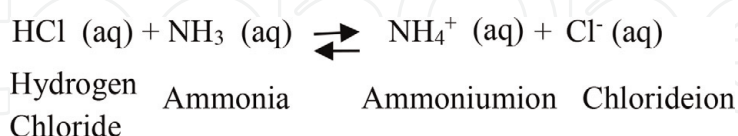
- Bronsted-Lowry acid-Hydrogen ion (Proton) donor.
- Bronsted-Lowry base-Hydrogen ion (Proton) acceptor.

9.1 Conjugate acid-base pairs

- Conjugate acid: It forms when a base accepts proton.
- Conjugate base: It forms when an acid donates proton.

Note: If an acid is strong, the conjugate base will be weaker and if the base is strong, the conjugate acid will be weak.

Consider the following chemical reaction:



In this reaction, HCl is an acid because it is donating proton to NH₃. Therefore, HCl is act as Bronsted-Lowry acid whereas NH₃ has a lone pair of electrons which is used to accept the protons. Therefore, NH₃ is act as Bronsted-Lowry base. This reaction is reversible also. In reversible case, the ammonium ion reacts with chloride ion and again converts into ammonia (NH₃) and hydrogen chloride (HCl). In this case, the ammonium ion is donating a proton, called conjugate acid. The chloride ion (Cl⁻) ion is accepting a proton, called conjugate base.

There are two conjugate pairs—conjugate pair 1 and conjugate pair 2.

Conjugate pair 1: HCl and Cl⁻

Conjugate pair 2: NH₃ and NH₄⁺

From that equation, the ammonium ion (NH₄⁺) is a conjugate acid of base ammonia and chloride ion (Cl⁻) is a conjugate base of acid hydrogen chloride.

Note: According to the theory of Arrhenius, the reaction between HCl and NH₃ is not considered as acid-base reaction because none of these species gives H⁺ and OH⁻ ions in water.

9.2 Examples of Bronsted-Lowry acids and bases



In this reaction, the nitric acid donates a proton to the water, therefore it act as a Bronsted-Lowry acid. Since, water accepts a proton from nitric acid, so it is act as Bronsted-Lowry base. In this reaction, the arrow is drawn only to the right side which means that reaction highly favours the formation of products.



In this reaction, the water is losing its proton, becomes hydroxide (OH⁻) and donates its proton to the ammonia. Therefore, water is act as Bronsted-Lowry acid. Ammonia is accepting a proton from the water, forms ammonium ion (NH₄⁺). Therefore, ammonia is act as Bronsted-Lowry base.

From the above two reactions, we can conclude that the water is Amphoteric in nature which means that it can act as both: Bronsted-Lowry acid and Bronsted-Lowry base.

9.3 Advantages of Bronsted-Lowry theory

1. This theory is able to explain the acid-base behavior in aqueous and non-aqueous medium.

2. It explains the basic character of substances like NH_3 , CaO , Na_2CO_3 , that is, which do not contain $-\text{OH}$ group but according to Arrhenius theory, they are not considered as bases.
3. It explains the acidic character of substances like CO_2 , SO_2 , etc. which do not contain hydrogen ion group but according to Arrhenius theory, they are not considered as acids.
4. This theory also explains the acid-base behavior of ionic species.

9.4 Disadvantages of Bronsted-Lowry theory

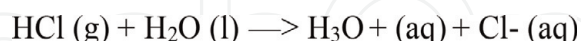
1. According to Bronsted-Lowry theory, same compound is act as acid in one reaction and act as base in other reaction. So, sometimes it is very difficult to predict the exact acid or base in a reaction.
2. This theory is not able to explain the acidic, basic as well as Amphoteric gaseous molecule.
3. This theory does not explain the behavior of acids like BF_3 , AlCl_3 , BCl_3 , etc. which do not protons to loose or donate.
4. This theory does not explain reactions between acidic oxides (CO_2 , SO_2 , SO_3) and basic oxides (CaO , MgO , BrO) which takes place in the absence of solvent.

10. Relation between Arrhenius theory and Bronsted-Lowry theory

These two theories are not against to each other in any way, in fact Bronsted-Lowry theory is advance to the Arrhenius theory.

According to the Arrhenius theory, a substance which produces hydrogen ion in water, called acid. A substance which produces hydroxide ion in water, called base.

According to Bronsted-Lowry theory, an acid is proton donor and base is proton acceptor.



According to Arrhenius theory, hydrochloric acid is an acid which gives hydrogen ions in water but according to Bronsted-Lowry theory, hydrochloric acid is an acid because it donates a proton to the water molecule. By observing both concepts, water is acting as a base. So, we can see here that both theories are very similar to each other.

Actually, Arrhenius theory is limited only to the aqueous solution. It does not explain the acid behavior in gaseous form.

11. Lewis acid-base theory

The Bronsted-Lowry theory which we have been previously studied was a good startup for acid-base chemistry. The Bronsted-Lowry concept was based on the transfer of proton from one chemical species to another. But this theory has certain limitations. UC Berkeley scientist, G.N. Lewis, in 1923 proposed a new acid-base theory which is based on their transfer of electrons. This theory is more advanced

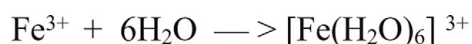
and flexible than Bronsted-Lowry because it explains the acid-base behavior in that molecules which do not contain hydrogen ions or in non-aqueous medium.

11.1 Lewis acid

According to this theory, an acid is a substance which has capability to accept the non-bonding pair of electrons, called Lewis acid. They are sometimes referred as electron deficient species or electrophile.

11.1.1 Lewis acid: characteristics

- Lewis acid-electron-pair acceptor.
- Lewis acid should have a vacant or empty orbital.
- All cations (Na^+ , Cu^{2+} , Fe^{3+}) are Lewis acids because they have capability to accept a pair of electrons but all Lewis acids are not cations.



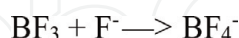
Metal cation having	Lone pair present
positive charge and	on oxygen
empty orbital	

More is the positive charge on the metal, more is the acidic character. Fe^{3+} is good Lewis acid than Na^+ .

- The ion, molecule or an atom which has incomplete octet of electrons are also Lewis acids.

For example: BF_3 .

Here, you can see that the central atom boron has six electrons in its outermost shell. So, it has ability to accept more electrons due to the presence of an empty orbital and hence, act as Lewis acid.



- The molecule in which the central atom has more than eight electrons (SiF_4 , SiBr_4), are also considered as Lewis acids.
- The molecule like CO_2 , SO_2 , etc. are also considered as Lewis acid. These types of molecules form multiple bond between the atoms of different electronegativity. In case of transition metal ions, the metal having more electronegativity makes stronger Lewis acids.
- Electron poor π : system is also considered as Lewis acids, for example, $[\text{CH}_2=\text{CH}]^+$, etc.

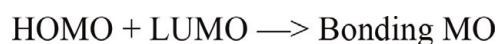
11.2 Lewis base

A base is a substance which has capability to donate the electrons, called Lewis base. They are sometimes referred as electron rich species or Nucleophile.

11.2.1 Lewis base: characteristics

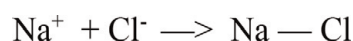
1. Lewis base-electron-pair donor
2. All metal anions (F^- , Cl^- , Br^- , I^-) are Lewis base because they have ability to donate the electron but all Lewis bases are not anions.
3. The ion, molecule or an atom which having a lone pair of electrons, are also considered as Lewis base.
4. The electron-rich π system is also considered as Lewis bases, for example, benzene, ethene, etc.
5. The strength of the Lewis base can be increased by increasing the electron density.

Note: When a Lewis acid reacts with Lewis base, then Lewis acid uses its lowest unoccupied molecular orbital (LUMO) and base uses its highest occupied molecular orbital (HOMO) to create a bonded molecular orbital. Actually, Lewis acid and Lewis base both have LUMO and HOMO but HOMO is always considered as base and LUMO is always considered as acid.



11.3 Example of Lewis acid-base

A simplest example of Lewis acid-base is shown by a chemical reaction:



In this reaction, chloride ion acts as Lewis base because it has lone pairs of electrons and sodium ion has positive charge, so it acts as Lewis acid.

11.4 Neutralization reaction between Lewis acid and Lewis base

When a Lewis acid reacts with a Lewis base, then a Lewis acid-base reaction occurs in which the molecule which act as Lewis base donate its electron pair into the empty orbital of an acid, forms Lewis acid-base adduct as shown in **Figure 2**. The adduct formed contains a covalent coordinate bond between Lewis acid and Lewis base. The above explanation implies that the Lewis acid is a low electron density centre and Lewis base is a high electron density centre [6].

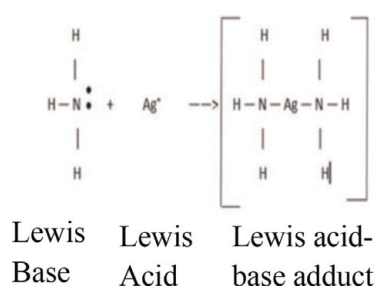


Figure 2.
 Acid-base neutralization.

In this reaction, the two ammonia molecules react with silver ion. The ammonia has lone pair of electrons, so it has the ability to donate the lone pairs of electrons and acts as Lewis base. The positive charge on silver denotes its electrophilic nature that means it has an ability to accept the pairs of electrons and act as Lewis acid (by Lewis definition).

Here, it can also be noted that when a Lewis acid reacts with a Lewis base, there is no change in the oxidation number of any of these atoms.

11.5 Limitations of Lewis acid-base theory

1. This theory is not able to explain that why all acid-base reactions do not involve the covalent coordination bond.
2. This theory is also unable to explain the behavior of some acids like hydrogen chloride (HCl) and sulfuric acid (H₂SO₄) because they do not form the covalent coordination bond with bases. Hence, they are not considered as Lewis acids.
3. This theory cannot explain the concept that why the formation of coordination bond is a slow process and acid-base reactions is a fast process.
4. This theory cannot explain the concept of relative strength of acids and bases.
5. This theory fails to explain the catalytic activity of some Lewis acids.

12. Relation between Lewis acid-base theory and Arrhenius theory

1. All Arrhenius acids and Bronsted Lowry acids are Lewis acids but reverse is not true.

13. Conclusion

Acids and bases are very important for modern society and in our daily lives. They exist everywhere in our body and in our surroundings. The theory that has been described in this chapter has given us all the basic information of acids and bases. In this chapter, we have discussed all the three basic theory of acid-base chemistry-Arrhenius theory, Bronsted-Lowry theory and Lewis acid-base theory. Acids and bases have vital role in the area of medicine. From this concept, it is now easy to treat the diseases with the improved medicines by complex understanding of acids and bases. For example, If the concentration of hydrogen ion increases in the human blood, acidity increases that results weakness in body. In that condition, the body should keep alkaline by digesting food that produces alkali in the body, to neutralize the acidity.

Definitely, without acids or bases information, our lives would look different to how it looks now. Many products we are using today would have no use without this knowledge.

Acknowledgements

I am eternally grateful and beholden to my family. My mother Mrs. Suman Munjal, Father Mr. Bhim Sain Munjal and sister Mrs. Shweta Java for strengthening

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Conflict of interest

None.

Declaration

I Shikha Munjal undersigned solemnly declare that all the information submitted by me in this chapter is correct, true and valid.

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